Soft X-ray absorption spectroscopy of *single* nanocrystals

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INTRODUCTION

The development of the electronic structure of nanocrystals and the investigation of size dependent scaling laws is an active research area of academic and technological relevance [1,2]. In general, experiments are performed on ensembles of nanocrystals which, even in the best samples, still exhibit a distribution with respect to particle size and shape, crystallinity and defect structure etc. In consequence, scaling laws derived from such experiments represent an ensemble average with an inherent uncertainty with respect to intrinsic properties of individual nanocrystals. To overcome these limitations, single particle experiments have been developed and performed in recent years [3-5]. For instance, in optical fluorescence spectroscopy of ensembles of semiconductor nanocrystals one observes typically rather broad fluorescence lines (FWHM ~0.1-0.2 eV at 10 K). However, experiments on individual nanocrystals yield not only extremely sharp emission lines (FWHM ~200 μeV at 10 K) but also allow the observation of effects like spectral diffusion and blinking of single nanocrystals which is inherently not possible with ensemble techniques [3].

While the size dependence of the optical excitation gap can be investigated with optical spectroscopy, detailed information about the electronic structure can be obtained by X-ray absorption spectroscopy (XAS) [6]. In addition, insight into the chemical composition, structural properties, and even the magnetic properties of nanostructures can be obtained. Here we report the first experiments to explore the feasibility of spectromicroscopy to record the X-ray absorption spectra of a *single* nanocrystal using photoelectron emission microscopy (PEEM). The experiment was carried out with the PEEM2 instrument of the Advanced Light Source at beamline 7.3.1.1 [7].

EXPERIMENT

PEEM combines two concepts: X-ray absorption spectroscopy and electron microscopy. The currently best spatial resolution achieved is 20 nm. Although this is not sufficient to resolve a nanocrystal (typical size 2-15 nm) the spectrum of a single nanocrystal can be obtained if the mean interparticle distance is larger than the spatial resolution and the area between the particles contribute as little as possible to the overall signal. For the initial experiments, iron oxide nanocrystals (γ-Fe_2O_3, maghemite [8]) with a mean diameter in the range of 6 to 13 nm were deposited on different substrates with varying coverage. The actual coverage was measured with transmission (TEM) or scanning electron microscopy (SEM).

Figure 1a shows the SEM image of iron oxide nanocrystals (13 ± 2 nm) spin-coated onto graphite (HOPG). The image shows randomly distributed bright spots and, occasionally, spots arranged in lines. The latter are formed by nanocrystals aligning themselves at steps on the graphite surface. High-resolution SEM imaging (not shown) reveals that those spots correspond to agglomerates of about 4-30 nanocrystals. The average distance between the bright spots is around 250 nm and is therefore sufficiently bigger than the typical spatial resolution of PEEM to allow X-ray absorption

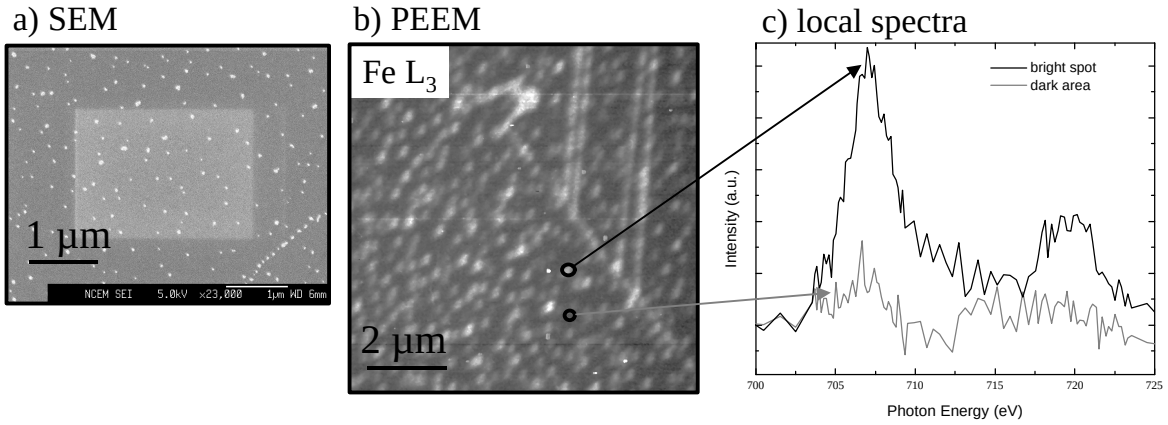

Figure 1: a) Scanning electron microscope image of iron nanocrystals on graphite. The image shows randomly distributed spots and spots arranged in lines. The spots consist of agglomeration of 4-30 nanocrystals. The Photoemission electron microscope image (b) recorded at the iron L_3 resonant absorption edge shows a similar arrangement of bright spots. The spectrum recorded from one bright spot and from a dark area is shown in (c).

spectroscopy of those individual spots. A similar image is obtained with PEEM tuning the photon energy to the L_3 resonant absorption edge of iron at 707 eV, see Figure 1b. Though it was not possible to record the spectra of a single nanocrystal, since all nanocrystals assembled into small agglomerates upon deposition, we were successful to measure the X-ray absorption spectra of ensembles of 4 –30 iron oxide nanocrystal. The spectrum recorded from one bright spot (see Figure 1c) shows the typical $L_{3,2}$ features of iron oxide [9] whereas they are absent in the spectrum of the dark area, which clearly demonstrate that the spots in the PEEM image are from the iron oxide nanocrystals.

In the future, we will further explore different substrates and sample preparation techniques and work on the signal to noise ratio of the PEEM images. This project will benefit from the development of an aberration corrected PEEM (PEEM3) which is currently being designed at the ALS. Besides the higher spatial resolution of PEEM3, this project will strongly benefit from the higher transmission increasing the signal to noise ratio.

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[9] The multiplet structure is hardly resolved due to the moderate energy resolution of the beamline.